Dissociation Constants and Conductivities of HCl and DCl in *N,N*-Dimethylformamide at 25°C

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The thermodynamic dissociation constants for HCl and DCl in *N,N*-dimethylformamide (DMF) are obtained at 25°C from conductance data. The values of the dissociation constants on the molarity composition scale are (2.68 ± 0.03) × 10^{-4} and (2.64 ± 0.02) × 10^{-4} for HCl(DMF) and DCl (DMF), respectively. The values of the limiting molar conductances for HCl(DMF) and DCl(DMF) are 79.85 ± 0.82 and 79.00 ± 0.62 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$, respectively.

This paper reports our results for the molar conductivities and the thermodynamic dissociation constants for HCl and DCl in *N,N*-dimethylformamide (DMF) at 25°C. The reactions that were studied are

$$\text{HCl(DMF)} = \text{H}^+\text{(DMF)} + \text{Cl}^-\text{(DMF)} \qquad (1)$$

$$\text{DCl(DMF)} = \text{D}^+\text{(DMF)} + \text{Cl}^-\text{(DMF)} \qquad (2)$$

The equilibrium constants for Reactions 1 and 2 can be combined to obtain the equilibrium constant for the homogeneous, isotope-exchange reaction

$$\text{HCl(DMF)} + \text{D}^+\text{(DMF)} = \text{DCl(DMF)} + \text{H}^+\text{(DMF)} \qquad (3)$$

The value of K for Reaction 3 has been predicted on the basis of electrochemical cell measurements as K_3 = 1.02 ± 0.04 (*8*). The predicted value of K_3 is in agreement with the ratio K_1/K_2 obtained from the results of this conductance study.

Experimental

The method of preparation of anhydrous DMF and anhydrous HCl(DMF) and DCl(DMF) solutions on the vacuum line has been described (*8*). The conductance cell was connected directly to the vacuum line by 10/30 ₸ joints (*9*) and filled with the appropriate solution under a nitrogen atmosphere. The cell was then closed off, removed from the line, and placed in the constant-temperature oil bath.

The conductance measurements were made with a Leeds and Northrup #4666 Jones conductance bridge. The power for the Jones bridge was provided by a Hewlett-Packard 0201-C audiofrequency oscillator. The null detector used was a General Radio Co. 1232A tuned amplifier-null detector. A Tektronix 564B oscilloscope was also used to aid in the detection of the null point. A General Radio Co. 1419-M decade capacitance box was used as the external bridge capacitor. The constant-temperature oil bath was made in this laboratory (*9*). This bath is equipped with a sump-type oil recirculation and heating system and a solid-state proportional temperature controller (designed and built by David Jenkins, UCD). The bath temperature was easily controlled to 25.000 ± 0.001°C and was monitored with a Leeds and Northrup #8163 four-lead, certified platinum resistance thermometer. The thermometer resistance was measured with a Leeds and Northrup 8069-B Type G-2 Mueller Bridge.

The conductance cell was a Leeds and Northrup Model 4942. The cell electrodes were smooth, shiny platinum. The cell constant was determined by the standard method by use of KCl(aq) data of Jones and Bradshaw (*4*) corrected to absolute ohms. The conductance water used to prepare the KCl(aq) solution had a specific conductance of 0.6 × 10^{-6} $\text{ohm}^{-1}\ \text{cm}^{-1}$. The cell constant was determined several times throughout the course of the work; the average value was 0.034511 ± 0.000005 cm^{-1}.

The resistance of a particular solution of HCl(DMF) or DCl(DMF) was measured at 1-kHz intervals over the frequency range 2–20 kHz. The reported cell resistance was taken as the average of the resistance values over the range 5–10 kHz, as recommended by Hoover (*3*). For frequencies in the range 5–10 kHz, the resistance of a given solution varied from ±0.20 ohm or less for the most concentrated solutions to ±2.0 ohm or less for the most dilute solutions. Solutions resistances at a given frequency were stable to better than ±0.1 ohm for 24 hr.

The concentrations of the HCl(DMF) and DCl(DMF) solutions were determined electrochemically by use of cells of the type

$$\text{H-glass}|\text{HCl} + \text{KNO}_3 \text{ in } \text{H}_2\text{O} + \text{DMF}|\text{Hg}_2\text{Cl}_2\text{(s)}|\text{Hg(l)} \qquad (4)$$

where H-glass is a Beckman E-2 hydrogen-ion glass electrode, and the calomel electrode was prepared according to the method of Hills and Ives (*2*). The reference solution for the cell (Equation 4) consisted of an approximately 2 × 10^{-3} *M* HCl which was prepared by diluting constant-boiling HCl(aq) with a mixture of H_2O and DMF so that the final solution consisted of 9.0 parts water to 1.0 parts DMF. The ionic strength of the reference solution was adjusted to 0.120 by addition of KNO_3(s). Solutions from the conductance cell were analyzed as follows: 10.00 ml of cell solution was measured out from a 10-ml buret into 90.0 ml of an aqueous KNO_3 solution with an ionic strength of (0.120 × 100/90). The resulting solution was placed in the emf cell, and the voltage of the cell was determined with a Beckman Research pH meter. The ratio of HCl concentrations in the test and reference solutions is readily calculated from the difference in voltage readings

$$\epsilon_x - \epsilon_{\text{ref}} = -\frac{RT}{F} \ln \frac{[(\text{H}^+)(\text{Cl}^-)]_x}{[(\text{H}^+)(\text{Cl}^-)]_{\text{ref}}} \qquad (5)$$

where the activity coefficients cancel because the ionic strengths are equal. The actual concentration HCl(DMF) in the conductance cell is 10 times that in the emf cell. The emf of the cells was stable to 0.1 mV, and this corresponds to an uncertainty in the concentration of about 0.5%. Because the mole percent of deuterium in the emf cell solution obtained from the DCl(DMF) conductance cell solutions is negligible after dilution with 90 ml of water, the D for H isotope effect on the voltage of the emf cell was ignored.

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Results

Values of the molar conductances of HCl(DMF) and DCl(DMF) solutions are given in Table I. The molar conductance was calculated from the expression

$$\Lambda = \frac{(a/R - k_s')1000}{M} \tag{6}$$

where a is the cell constant, R is the resistance of the solution having molarity M, and k_s' is the specific conductance of the solvent. The value of k_s' was determined for each batch of purified solvent that was used to make solutions. The values of k_s' fell in the range of 0.7–2 × 10^{-7} ohm^{-1} cm^{-1}.

The equilibrium constant K for Reaction 1 is given by (*5*)

$$\ln K \simeq \ln\left(\frac{\Theta^2 M}{1 - \Theta}\right) - \frac{2A(\Theta M)^{1/2}}{1 + (\Theta M)^{1/2}} \tag{7}$$

where Θ is the degree of dissociation of HCl in a DMF solution in which the total concentration of HCl is M, and A is the Debye-Hückel parameter; $A = 3.566$ for DMF at 25°C.

The conductance data were evaluated by means of the Shedlovsky equation (*1, 7*)

$$\Lambda = \Theta\Lambda_0 - \alpha(\Lambda/\Lambda_0)(M\Theta)^{1/2} \text{ where } \Theta = S\Lambda/\Lambda_0 \tag{8}$$

where

$$S = \{z/2 + [1 + (z/2)^2]^{1/2}\}^2; \text{ and } z = \frac{\alpha(\Lambda M)^{1/2}}{\Lambda_0^{3/2}} \tag{9}$$

For DMF at 25°C the Onsager coefficient is $\alpha = 0.7165\Lambda_0 + 99.07$.

Initial values of Λ_0 were obtained from the (least-squares) intercepts of plots of $1/\Lambda$ vs. ΛM ($1/\Lambda = 1/\Lambda_0 + M\Lambda/K\Lambda_0^2$). These initial Λ_0 values were used to compute $1/\Lambda S$ and $M\Lambda S f_\pm^2$, where $f_\pm$ is the mean ionic activity coefficient $f_\pm \simeq \exp\{-A(\Theta M)^{1/2}\}$; a refined Λ_0 value was then obtained from the (least-squares) intercept of a plot of $1/\Lambda S$ vs. $M\Lambda S f_\pm^2$,

$$1/\Lambda S = 1/\Lambda_0 + M\Lambda S f_\pm^2/K\Lambda_0^2 \tag{10}$$

This value of Λ_0 was used in turn to obtain a new Λ_0 value; Λ_0 converged to a constant value (to 0.01%) in three cycles. Shedlovsky plots of the data in Table I are shown in Figure 1. The final value of Λ_0 was used together with Equation 7 to find ln K, as the (least-squares intercept of a plot of $\ln(\Theta^2 M/1 - \Theta)$ vs. $(\Theta M)^{1/2}/[1 + (\Theta M)^{1/2}]$. The least-squares fitted slopes of these plots are 7.34 ± 1.20 and 6.67 ± 0.99 for HCl(DMF) and DCl(DMF), respectively, compared to a theoretical slope of 7.13. The intercepts of the plots gave the following K values for Reactions 1 and 2:

$$K_1 = (2.68 \pm 0.03) \times 10^{-4} \qquad (\Lambda_0 = 79.85 \pm 0.82)$$

$$K_2 = (2.64 \pm 0.02) \times 10^{-4} \qquad (\Lambda_0 = 79.00 \pm 0.62)$$

The values of K are consistent with the values for K_1 and K_2 obtained directly from the slopes of the Shedlovsky plots, namely, $K_1 = (2.68 \pm 0.08) \times 10^{-4}$ and $K_2 = (2.61 \pm 0.04) \times 10^{-4}$.

Discussion

The values for K_1 and K_2 obtained in this study yield an equilibrium constant for the homogeneous, hydrogen isotope-exchange reaction (Reaction 3) of $K_3 = 1.02 \pm 0.04$. This result is a completely independent check of the value of $K_3 = 1.02$ predicted on the basis of emf results (*8*) for hydrogen isotope-exchange reactions of the type

$$D_2(g) + 2HCl(DMF) = H_2(g) + 2DCl(DMF)$$

The only other moderate-to-high precision studies of conductivities in DMF are found in papers of Thomas and Rochow (*10*) and Prue and Sherrington (*6*). Thomas and Rochow report a dissociation constant for HCl in DMF of (2.83×10^{-4}) ($\Lambda_0 = 79.3$) at 20°C. This value of K at 20°C was obtained from an Ostwald dilution law plot. We have reanalyzed the data of Thomas and Rochow in terms of the Shedlovsky equation. Our calculations yield a Λ_0 value of 83.42 ohm^{-1} cm^2 mol^{-1} and an equilibrium constant of $(2.33 \pm 0.04) \times 10^{-4}$ at 20°C. Combination of this result with our K value at 25°C leads to an estimate of $\Delta H° \simeq 20$ kJ mol^{-1} for the dissociation reaction.

That the Λ_0 values of LiCl, $NaClO_4$, $KClO_4$, KBr, and KI lie in the range 80–85 ohm^{-1} cm^2 mol^{-1} (*6*) suggests that the mobility of the proton in DMF ($\Lambda_0 \approx 80$ for HCl

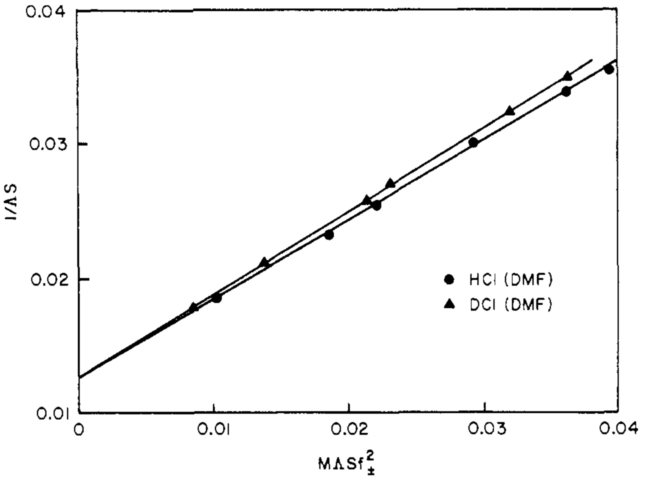

Figure 1. Shedlovsky plots for HCl and DCl at 25°C. Least-squares intercepts yield Λ_0 values of 79.85 ± 0.82 and 79.00 ± 0.62 ohm^{-1} cm^2 mol^{-1} for HCl and DCl, respectively

Table I. Conductance Data for HCl(DMF) + DCl(DMF) Solutions at 298.15K[a,b,c]

$M \times 10^4$, mol dm^{-3}	R, ohm	Λ, ohm^{-1} cm^2 mol^{-1}
	HCl(DMF)	
16.64	755.66 ± 0.16	26.94
14.47	826.14 ± 0.16	28.30
10.24	1025.93 ± 0.26	32.04
6.404	1372.92 ± 0.39	37.95
4.915	1623.47 ± 0.21	41.56
2.107	2903.39 ± 0.43	52.46
	DCl(DMF)	
14.98	838.11 ± 0.33	27.40
12.19	951.72 ± 0.14	29.62
7.131	1349.28 ± 0.16	35.67
6.251	1461.27 ± 0.70	37.56
3.248	2293.25 ± 0.48	45.90
1.644	3763.01 ± 1.61	54.92

[a] Conductance cell constant was 0.034511 ± 0.000005 cm^{-1}.
[b] The Λ values are corrected for the conductance of the solvent.
[c] All the errors quoted in the table (and elsewhere in the text) are standard deviations.

in DMF) is essentially the same as for the alkali metal ions. The available conductance, emf, and spectroscopic data (*8*) suggest that the proton in *N,N*-dimethylformamide is strongly solvated by a single DMF molecule and that a Grotthus-type conduction mechanism is not operative for the solvated proton in DMF.

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ORGANIC SECTION

Preparation and Properties of 1-Benzyloxy-3-arylureas, 1-Benzyloxy-3-alkylureas, and 1,5-Diphenyl-3-benzyloxybiuret

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Preparation and properties of 15 1-benzyloxy-3-arylureas, two 1-benzyloxy-3-alkylureas, and 1,5-diphenyl-3-benzyloxybiuret are described.

Preparation and properties of 15 1-benzyloxy-3-arylureas, represented by the general formula I, are reported here. These were prepared to study their oxidation with lead tetraacetate which, in general, gave 1-benzyloxybenzimidazolones or 1,2-dibenzyloxy-1,2-diarylcarbamylhydrazines (*2, 3*).

$$C_6H_5CH_2ONHCONHAr$$

I

The preparations were carried out by reaction of aryl isocyanate with benzyloxyamine, a reaction first described by Voltmer (*2*). Benzyloxyamine hydrochloride was prepared by a modification of the procedure used by Mamalis et al. (*7*), treatment of *N*-acetylbenzyloxyamine with ethanol saturated with hydrogen chloride. Benzyloxyamine was isolated by ether extraction of an aqueous alkaline mixture of the amine hydrochloride. The amine was then allowed to react with equimolar amounts of phenyl isocyanate.

When an equimolar quantity of benzyloxyamine was added to phenyl isocyanate (*8*), two products were obtained and were separated by column chromatography on alumina. The second product to be eluted with methanol was the desired 1-benzyloxy-3-phenylurea. The first product was eluted with ether and was shown by elemental analysis to be an addition product of 2 moles of phenyl isocyanate with 1 mole of benzyloxyamine. Such a reaction product was described by Kjellin and Kuylenstjerna (*5*) with a reported melting point of 240°. However, our product had an observed melting point of 140°. The proposed structure of this product is II, and to prove this, II was hydrogenated at 2 atm pressure, room temperature, and with a Raney nickel catalyst. The product mp 209–210° was identical to 1,5-diphenylbiuret (*4, 6*) by ir and mixed melting point.

$$C_6H_5NHCON(OCH_2C_6H_5)CONHC_6H_5$$

II

Alternately, when an equimolar amount of aryl isocyanate was added slowly to benzyloxyamine to keep the benzyloxyamine in excess until the last of the isocyanate was added, only the urea product was isolated. Finally, when the benzyloxyamine was added to a 4*m* ratio of phenylisocyanate, only 1,5-diphenyl-3-benzyloxybiuret was isolated.

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